EFFECT OF WATER ON CP/MAS ^{13}C NMR SPECTRA OF LOW-RANK COALS

Sylvia A. Farnum, Donald D. Messick and Bruce W. Farnum

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Studies are being carried out directed toward elucidating the structure of low-rank coals and the mechanisms of their combustion, gasification, slurry preparation and liquefaction at the University of North Dakota Research Center. As a part of this research, our interest in the carbon structure of coals before and of residues after processing led us to develop solid ^{13}C CP/MAS NMR techniques suitable for our samples. As we surveyed the existing literature (1,2,3) and the results obtained in our laboratory for low-rank coals, we noted apparent intensity discrepancies. Some samples gave stronger signals than others when the same amount of carbon was in the rotor. In addition to variable intensities, the aromatic to aliphatic ratios and the relative intensities of prominent peaks varied for duplicate samples run under the same conditions. The effect of mineral matter in the high ash coals or the effect of free radicals in the coal were suggested as possible causes of these difficulties (4,5). However, in the case of our samples, these explanations failed to account for the variability we saw in samples. We had none of these problems obtaining spectra of the insoluble organic matter (IOM) after liquefying these coals, even though the IOM contained up to 70 weigh percent ash and was greater than 90% aromatic carbon. Signals from the IOM samples were apparently proportional to the amount of carbon present and did not vary.

We had already optimized all of the variables required by our intial study. Each variable was important and needed to be carefully assessed directly on the coal samples to be used for further work. The work of many investigators emphasizes that when proper care is exercised, representative coal spectra may be obtained (1,6,7,8,9). Our conclusions were in accord with those previously reported with one important exception. For low-rank coals, peats and other solids that contain more than a trace of moisture, this study shows that the presence of moisture is the overwhelming factor in determining spectral intensity.

Experimental

Our NMR work was carried out at 50.3 MHZ using our Varian XL-200 NMR. A Doty Scientific, Inc. high sensitivity carbon solids probe was interfaced directly with the standard Varian solids amplifier. The magic angle was adjusted for minimal line width with hexamethylbenzene, the probe was tuned for the decoupler and the observe signal with the coal sample in the probe, the field was centered and shimmed, the power level of the decoupler was accurately set, the 90° and 180° flip angles were adjusted (+0.1μs), the contact time for cross-polarization was selected to best fit the $T1\rho$ values for the coal and an appropriate delay was chosen. The pulse sequence used was a typical cross-polarization experiment which provided an accurate 90° flip for the proton reservoir followed by a 90° proton phase alteration (spin-lock). The contact time, 1ms, fulfilling the Hartmann-Hahn condition ($\gamma_H H_{1H} = \gamma_C H_{1C}$), was followed by four timed 180° pulses of the TOSS echo sequence to refocus the spinning sidebands back into the isotropic peak(10). The acquisition of 4 K data points was carried out with high power proton decoupling. The selected recycle time was 1 s. Minimal data enhancement, consisting of 15 Hz line-broadening, apodization function of 0.020 was used.

Results and Discussion

Intrinsic water in low-rank coals plays a role in reactivity that has never been properly defined. It became apparent to us that water was also important in solid CP/MAS 13C NMR spectroscopy. We found little in the literature that addressed the practical aspects of this problem, therefore, we initiated a preliminary screening

of the effect. We selected two coals as representatives of low-rank coals in general, a North Dakota lignite from the Indian Head mine and a Texas lignite from the Big Brown mine (Table 1). A sample of each was divided into two portions. One portion was dried overnight under partial vacuum in a desiccator containing drierite. The other portion was retained as received. ASTM moisture determinations were run on these samples and on all other samples before ^{13}C spectra were acquired.

Table 1. Lignite Analyses

	Indian Head (ND)	Big Brown (TX)
Moisture, wt %	22.2	23.1
Proximate Analysis (wt. % dry basis)		
Ash	10.5	12.1
Volatile Matter	37.2	45.9
Fixed Carbon	52.3	42.0
Ultimate Analysis (wt/ % mf)		
C	68.1	63.1
H	4.5	4.6
N	1.2	1.3
S	0.9	1.0
O	14.8	17.9

The vacuum dried coal was loaded into a 7 mm sapphire cylindrical rotor and placed in the Doty probe. The rotor was spun at 3000 rps and introduced into the 47 KGauss field of our NMR. The observe and decoupler signals were carefully tuned before the sample spectrum was acquired using the optimized conditions for the dried coal sample. The dried sample was replaced by the same weight of the AR coal sample and another spectrum was acquired in exactly the same manner. The AR coal spectrum gave approximately 1/5 of the absolute intensity of the carbon spectrum of the dried coal. For the Indian Head Zap lignite, fa for the dried sample was 0.67 and for the AR sample, only 0.48 (Table 2).

Table 2. Indian Head Lignite Changes Due to AR Moisture Solid ^{13}C CP/MAS NMR Data

% H_2O	Absolute Intensity C Signal	% $C_{aromatic}$	% $C_{aliphatic}$
0	242.0	67.6	32.4
1.8	198.2	69.4	30.6
7.6	189.5	69.0	31.0
13.0	133.0	65.0	35.0
22.0 (AR)	50.7	47.7	52.3

A series of partially dried coal samples were prepared for comparison with the completely vacuum dried coal and the AR coal. The spectra of these samples recorded

at various moisture levels are presented in Figure 1. The absolute intensities for each spectrum and their apparent % C aromatic and % C aliphatic are given in Table 2.

It is apparent from these values that the presence of water detunes the probe. When an attempt is made to tune the observe and decoupler coil with the "wet" AR coal in the coil, it is seen that the capacitance of the coil is changed a great deal by the presence of the small amount of water. Modern commercial probe design does not allow for large changes in capacitance of the decoupler coil. Tuning the observe coil is possible but only with broad-band probes. Carbon-only probe observe signal variable capacitance cannot accomodate these large changes.

Even if the operator could optimize the critical tune of the decoupler coil for the cross-polarization, "correct" spectral intensities of "wet" AR coals could not be reliably obtained because under rapid rotation and high power ^{1}H decoupling, there is a small gradual drying of the coal. And, of course, as the coal changes even slightly in water content, detuning during acquisition causes a loss of signal intensity and introduces errors in the aromatic to alipahtic ratios (Figure 1, Table 2).

The capacitance changes observed for the coal appear to be dependent on the dielectric constants of the included liquid. Liquids of high dielectric, as is expected, cause the greatest changes in capacitance, hence in tune and signal intensity (Table 3). The values of ε (dielectric constant) are given for liquids external to the magnetic field.

Table 3. Dried Indian Head Lignite Changes Due to Added Liquid Solid ^{13}C CP/MAS NMR Data

Dried Coal + Liquid, %	Absolute Intensity C Signal	% $C_{aromatic}$	% $C_{aliphatic}$	ε
H_2O, 19.9	17.8	45.6	54.4	80,78
H_2O, 11.2	127.0	68.6	31.4	
D_2O, 22.0	18.4	44.6	55.4	78
Ethanol, 22.5	3.9	51.6	48.4	24
CCl_4, 20.0	20.0	68.1	31.9	2
i-Octane, 20.7	216.0	64.7	35.3	2

The capacitance (and dielectric constant) of the system are also temperature dependent. Changes in wet and dry coal spectra as the temperature is lowered are shown for one of the lignites (Big Brown) in Figure 2. The spectra are all recorded in the absolute intensity mode. Other factors also become important as the temperature is lowered (11), but it is obvious that great caution must be exercised in acquiring and interpreting the data.

From the investigation reported here, it appears that under the "best" conditions fairly representative, reproducible solid ^{13}C spectra of low-rank coal can be obtained from vacuum dried samples. The contact time that yields maximum intensity is near 1000 μs for the aromatic portion of both lignites and slightly shorter for the aliphatic portion. Thus, the selection of 1000 μs as the optimum contact time slightly favors the aromatic part of the spectrum. This positive effect is offset by some aromatic signal loss, estimated at <3%, during spinning sideband suppression (10). We are currently investigating the relationship between signal intensity and the amount of dry coal carbon in the rotor both by absolute intensity measurements and by internal standard spin-counting experiments. It appears that the dried coal samples give much better signal intensity relationships than coals containing small amounts of water.

Performing CP/MAS ^{13}C experiments with complex solid samples such as coal and peat is becoming more common. This technique has opened exciting new areas of structural investigation in coal science and will certainly continue to grow rapidly in popularity. The coal scientist will have to become thoroughly conversant with such concepts as the decoupler power requirements, 90 and 180° flip angles, $T_{1\rho}$ values for his samples, optimal cross polarization times, correct delay, spinning speed, presence of radicals, effect of coal ash and many other factors. As each new experiment is designed, new variables may be introduced. Each variable must be carefully scrutinized, particularly for obvious effects such as the one reported here. When a series of coal samples are compared, or when low-rank coal spectra are being acquired, the samples must be dry enough to allow tuning within the range of the NMR probe or erroneous intensities and fa values will result.

References

1. Wilson, M.A., Pugmire, R.J. and Grant, D.M., 1983, Org. Geochem. 5, 121-129.
2. VanderHart, D.L. and Retcofsky, H.L., Fuel, 1976.
3. Gerstein, B.C., Chow, C., Pembleton, R.G., and Wilson, M.A., J. Phys. Chem., 1977, 81, 565.
4. Yokono, T., Miyazawa, K., Sanada, Y. and Marsh, H., 1979, Fuel, 58, 896-897.
5. Wind, R.A., Trommel, J. and Smidt, J., 1980, Fuel, 58, 900-901.
6. Hagaman, E.W. and Chambers, R.R., 1985, American Chemical Society Fuel Div. Prepr. 30 (1), 188-191.
7. Perdue, E.M., 1984, Geochimica at Cosmochimica Acta, 48, 1435-1442.
8. Hatcher, P.G. "The Origin, Composition, Chemical Structure and Diagenesis of Humic Substances, Coals, and Kerogens as Studied by NMR", 1980, PhD dissertation, University of Maryland.
9 Miknis, F.P., Sullivan, M., Bartuska, V.J. and Maciel, G.E., 1981, Org. Goechem., 3, 19-28.
10. Dixon, W.T., Schaefer, J., Sefcik, M.D., Stejskal, E.O., and McKay, R.A., 1982, J. Magn. Reson., 49, 341-345.
11. Macho, V., Kendrick, R. and Yannoni, C.S., 1983, J. Magn. Reson., 52, 450-456.

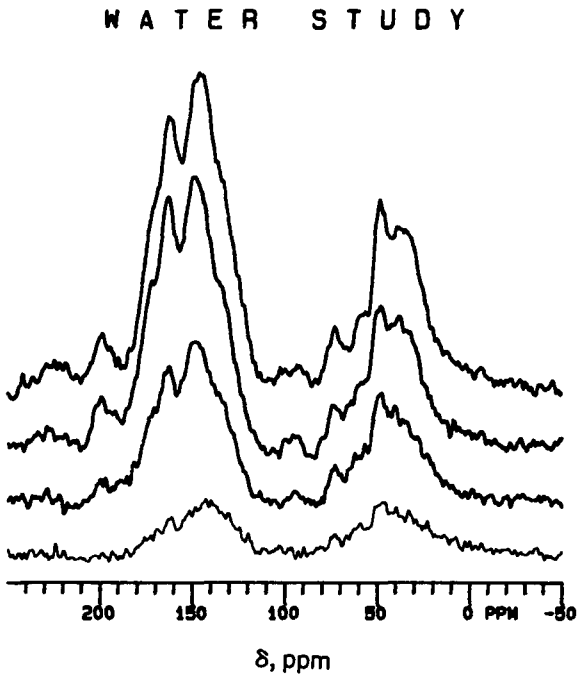

FIG. 1. Indian Head ^{13}C NMR Water study, top-dry, 2nd -7.6% water, 3rd, -13.0% water, bottom -22% (AR) water.

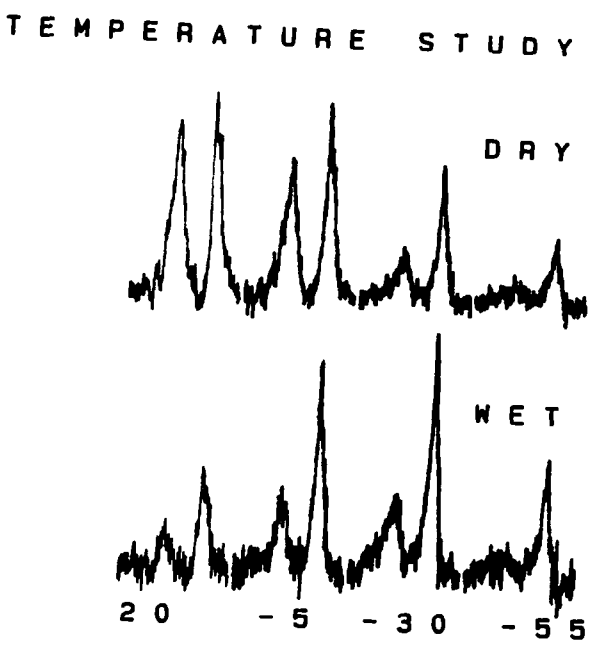

FIG. 2. Wet and Dry Big Brown lignite, ^{13}C NMR opectra at 20, -5, -30, and -55°C.